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Reactivity of 10-Thiaisoalloxazine. Ring-contraction by Water (Hydroxide Ion) followed by Redox Reaction.

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Heating of 3-methyl-10-thiaisoalloxazine (**1**) in aqueous acetonitrile results in the formation of 1,5-dihydro-3-methyl-10-thiaisoalloxazine (**3**), 1'-methylspiro〔2,3-dihydrobenzothiazole-2,5'-pyrimidine〕-2', 4', 6'-trione (**4**), and 1-(benzothiazol-2-yl) carbonyl-3-methylurea (**5**). In sharp contrast, 3,10-dimethylisoalloxazine (**2**) is very stable under the conditions employed. Experimental results document that the formation of (**3**) and (**5**) arises from a redox reaction between the ring-contracted product (**4**), initially produced by hydrolysis of (**1**), and unreacted (**1**). These reaction can be attributed to the increased susceptibility of (**1**) to nucleophilic addition and its higher oxidation capacity compared to the isoalloxazine (**2**).

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Photochemical Oxygenation of Phenols by Pyrimido[5,4-*g*]pteridine *N*-Oxide. Comparative Studies with Pyridazine and Isoalloxazine *N*-Oxides.

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1,3,7,9-Tetrabutylpyrimido〔5,4-*g*〕pteridine-2,4,6,8(1*H*, 3*H*, 7*H*, 9*H*)-tetrone 5-oxide (**1**) transfers its *N*-oxide oxygen to phenols, *i.e.*, phenol, *p*-cresol, *L*-tyrosine methyl ester, and *p*-hydroxyacetanilide (acetaminophen), under photochemical conditions to give the corresponding dihydric phenols as major products. The oxygenation is reasonably explained in terms of a photo-induced single-electron transfer (SET) followed by oxygen-atom transfer (the SET mechanism) which occurs *via* the initial formation of a charge-transfer complex between (**1**) and the phenols employed. Comparative experiments with 3,10-dibutylisoalloxazine 5-oxide and 3-methylpyridazine 2-oxide well demonstrate the simplicity and the mechanistic characteristics of the photochemistry of (**1**).

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Photo-oxygenation of Alkanes by a Heterocyclic *N*-Oxide *via* Nonoxene Mechanism. Peculiar Photochemical Property of Pyrimido[5,4-*g*] pteridine *N*-Oxide.

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Irradiation of a solution of cyclohexane (**2**) or adamantane (**3**) in chloroform containing pyrimido〔5,4-*g*〕pteridine *N*-oxide (**1**) with UV-visible light resulted in the formation of the corresponding oxygenated products〔cyclohexanol and cyclohexanone from (**2**); 1- and 2-hydroxyadamantanes and 2-oxoadamantane from (**3**)〕together with chlorinated products〔chlorocyclohexane and hexachloroethane (**4**) from (**2**); 1- and 2-chloroadamantanes and (**4**) from (**3**)〕. The present observation further demonstrates the peculiar photochemical property of (**1**) in comparison with the heterocyclic *N*-oxides so far investigated and indicates that an excited (**1**) functions as a radical initiator and an oxygen-atom donor to the non-activated alkanes in chloroform.